Hydroformylation of Oct-1-ene with Extremely High Rates using Rhodium Catalysts containing Bulky Phosphites

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A rhodium complex containing tris(*o*-*tert*-butyl-*p*-methylphenyl) phosphite as a ligand catalyses the hydroformylation of oct-1-ene with good selectivity and extremely high rates; the rate constant, which is pseudo first-order in $[H_2]$ and $1/[CO]$, shows that the reaction of hydrogen is the rate determining step.

The application of bulky phosphites in the rhodium catalysed hydroformylation has been a field of interest since the early 1980s[1] and addition of these ligands causes a high reactivity in the hydroformylation of otherwise unreactive alkenes. These type of ligands give rise to an active species containing only one bulky phosphite, resulting in the formula $RhH(CO)_3L$, as is evidenced by the *in situ* IR and NMR spectra.[2] This is in contrast to the proposed active species in the regioselective hydroformylation reaction, $RhH(CO)_2L_2$, in which L represents a phosphine[3,4] or a phosphite.[5,6] It was suggested that monophosphine complexes give lower regioselectivity than diphosphine complexes, using triphenylphosphine as a ligand.[3] The bulky phosphite containing catalysts were suggested not to be applicable for alk-1-enes, due to the high rates of isomerization that were found.[6]

We now report some striking results obtained in the hydroformylation of oct-1-ene with the use of a bulky phosphite. An extremely fast reaction was achieved, with a high linearity and a low rate of isomerization. Earlier measurements contradict our results probably on account of diffusion control.[5,6]

Hydroformylation of oct-1-ene was performed at 70–80 °C, using $Rh(CO)_2$(pentane-2,4-dionate) in the presence of a hundredfold excess of tris(*o*-*tert*-butyl-*p*-methylphenyl) phosphite as catalyst precursor. After bringing the autoclave and its contents under pressure and heating the catalyst solution to the reaction temperature, the alkene was added. Upon this addition the reaction started immediately as was evidenced by the pressure drop and a slight increase of the temperature. The reaction was stopped at a conversion of approximately 30%. The dependency on the partial pressures (p) of H_2 and CO and the reaction conditions are reported in Figs. 1 and 2.

The reaction rate increases with higher $H_2:CO$ ratios. The rate found for the formation of aldehydes at a $pH_2:pCO$ ratio of 5:1 was 85000 mol [mol Rh]$^{-1}$ h^{-1}. Even higher

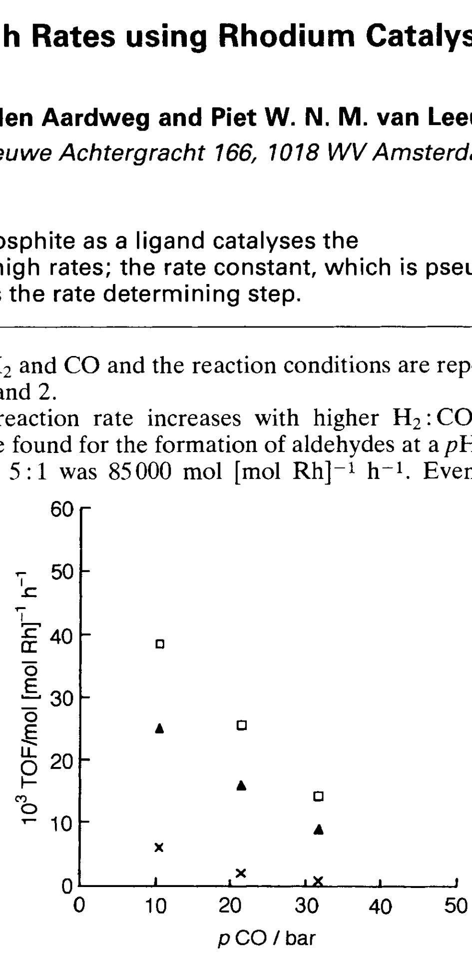

Fig. 1 Dependency of the rate of formation of aldehydes on CO pressure. TOF = turnover frequency, □, turnover frequency for all the aldehydes, ▲, turnover frequency for the normal aldehydes, ×, turnover frequency for the isomerization products. *Conditions*: T = 80 °C, pH_2 = 10 bar, $[Rh(CO)_2acac]$ = 0.1 mmol dm^{-3} $[(o\text{-}Bu^t\text{-}p\text{-}MeC_6H_4O)_3P]$ = 5 mmol dm^{-3}, [oct-1-ene] = 0.86 mol dm^{-3} in 20 ml of toluene, autoclave volume = 181 ml. During the reactions, samples were taken and analysed by gas chromatography. Experiments at lower CO pressures failed because of diffusion problems.

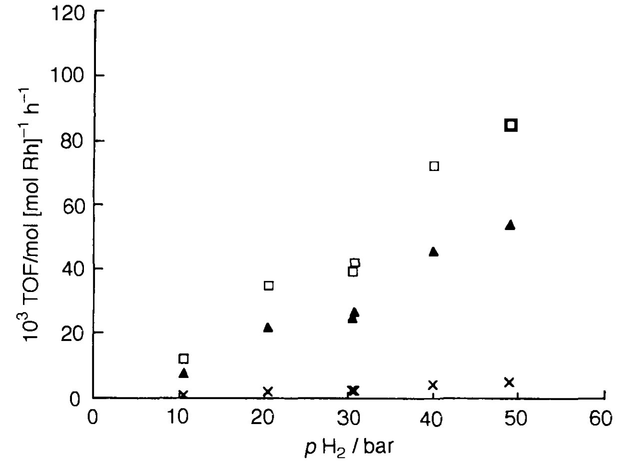

Fig. 2 Dependency of the rate of formation of aldehydes on H_2 pressure. TOF = turnover frequency, □, turnover frequency for all the aldehydes, ▲, turnover frequency for the normal aldehydes, ×, turnover frequency for the isomerization products. *Conditions: T* = 70 °C, pCO = 10 bar, [Rh(CO)$_2$acac] = 0.05 mmol dm^{-3} [(o-Bu^t-p-MeC$_6$H$_4$O)$_3$P] = 5 mmol dm^{-3}, [oct-1-ene] = 0.86 mol dm^{-3} in 20 ml of toluene.

rates were found at a total pressure of 80 bar, a reaction temperature of 80 °C and a H_2 : CO ratio of 7 : 1, *viz.* 161000 mol [mol Rh]$^{-1}$ h^{-1} (not shown in the graphs). The linear to branched ratio of the aldehyde product obtained was roughly 2 : 1 and the isomerization amounted to only 6%.

The graphs show an approximately pseudo first-order dependency on [H_2]/[CO]. A first-order dependency on the rhodium concentration was measured. Up to at least 30% conversion the rate was independent of the oct-1-ene concentration. The steric bulk of the ligand leads to the selective formation of a tricarbonyl species, RhH(CO)$_3$L, which has a strong aptitude for CO dissociation [as in RhH(CO)$_4$].[7] The 16e-intermediate reacts with substituted alkenes at a rate increasing with decreasing steric hindrance of the alkenes. The maximum rates are obtained with alk-1-enes where the overall rates are now independent of the alkene concentration. The negative order in CO explains the run-away character of the reaction at decreasing CO pressures and shows that, particularly owing to insufficient stirring of the reaction mixture, the diffusion of CO becomes rate determining. Absence of CO leads to fast isomerization of oct-1-ene, giving eventually a thermodynamic mixture of internal alkenes[6] or, because of the lower activity of the catalyst for the hydroformylation of internal alkenes, giving a slow hydroformylation reaction to mainly branched products[5] (the lower rate of hydroformylation for internal alkenes is attributed to steric effects).

The first order dependence in H_2 is also peculiar, as most phosphorus ligand modified rhodium catalysts are only very slightly effected by higher H_2 pressures.[8] The pressure dependencies indicate that the kinetics resemble those of the unmodified rhodium catalyst, RhH(CO)$_4$[9] *i.e.* that the rate determining step is the oxidative addition of H_2 to the Rh–acyl complex, which mechanistically may be either an oxidative addition[9] or a hydrogenolysis.[10]

Generally, the observed rates are at least 10 times higher than those observed for the Rh–triphenylphosphine catalyst,[11] while the selectivity and the low isomerization rate are retained.

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11 P. W. N. M. van Leeuwen and C. F. Roobeek, unpublished results, initial rate for the reaction of oct-1-ene in benzene 5% v/v, [Rh] = 0.5 mmol dm^{-3}, PPh$_3$: Rh = 10 : 1, 90 °C, p = 20 bar, CO : H_2 = 1 : 1 obtained was 5000 mol[mol Rh]$^{-1}$ h^{-1}. At very high PPh$_3$ concentrations the rate drops considerably. Rates reported in the literature are often lower by several orders of magnitude, *e.g.* D. Neibecker and R. Reau, *J. Mol. Catal.*, 1989, **57**, 153.